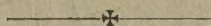
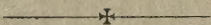


THE CARBON DIOXIDE MOLECULE ITS INFRARED SPECTRUM AND MECHANICAL STRUCTURE



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The Infrared Spectrum of Carbon Dioxide. Part I

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Previous work by Fermi and by Dennison has shown that the principal features of the infrared and Raman spectra of carbon dioxide may be explained by taking account of the first order perturbation terms in the potential energy expression. It was not possible to predict the positions of the levels with any high degree of accuracy, however. The present paper extends this work by introducing a second order perturbation. The formula for the second order energy correction of a general linear symmetrical triatomic molecule is initially computed. This formula is then modified in order that it may be applicable to the carbon dioxide molecule in which resonance degeneracy plays an essential rôle. A review is made of the experimental data which determine the positions of the carbon dioxide

vibrational energy levels. These include the results of a recent investigation of absorption bands appearing in the spectrum of Venus, as well as new and as yet unpublished data found by Barker and Wu. In all, twenty levels have been found and out of these, eleven are required to determine the anharmonic constants of the molecule. The remaining nine levels may then be predicted, and their positions are found to agree very accurately with the values obtained experimentally. A table is given showing the positions of a number of CO₂ infrared bands which while accessible to observation have not as yet been reported. The recent work by Langseth and Nielsen on the Raman spectrum of CO₂ is discussed.

INTRODUCTION

IT is now well known that the molecule of carbon dioxide possesses a form which is both linear and symmetrical, the carbon atom lying midway between the two oxygens. The group of normal vibrations of such a system constitute a zeroth order approximate solution to the motion which very satisfactorily explains the general features of the infrared spectrum of the molecule. The respective modes of vibration of the three independent frequencies are indicated schematically in Fig. 1.



FIG. 1.

The first of these ω_1 corresponds to a symmetrical motion of the oxygen atoms, the carbon atom remaining fixed at the center of mass. This frequency is inactive in the infrared, but will appear strongly in the Raman spectrum and lies at about 7.5μ . In the second frequency ω_2 the carbon

oscillates perpendicularly to the line joining the oxygen atoms, while the distance between the oxygens remains unchanged. ω_2 is a double frequency, active in the infrared, inactive in the Raman spectrum and lies at about 15μ . The unsymmetrical vibration with frequency ω_3 is a motion of the atoms along the figure axis of the molecule in which the carbon moves relative to the center of mass of the oxygens; where again the distance between the latter remains unaltered during the motion. This frequency which is active in the infrared and inactive in the Raman spectrum lies at about 4.7μ .

As has been remarked above, this model fully explains the principal observed features of the spectrum. When, however, the infrared and Raman spectra are examined more carefully, certain details appear which cannot be so simply understood. The Raman spectrum, for example, consists not of one line but of two lines of about equal intensity in the region of 7.5μ . Moreover, many of the combination bands in the infrared deviate from the positions predicted by combination relations by rather large amounts (i.e., approximately 100 waves per cm).

These difficulties have been completely explained by a theory proposed by Fermi¹ and

¹ E. Fermi, *Zeits. f. Physik* **71**, 250 (1931).

somewhat amplified by Dennison.² The explanation depends upon the fact that in carbon dioxide the frequency ω_1 is almost exactly equal to $2\omega_2$. The degeneracy thus introduced produces a first order perturbation which on the one hand changes the identity of the levels, allowing two Raman lines rather than one to appear. On the other hand, the perturbation yields a first order correction to the energy (of the order of 100 waves per centimeter) which accounts for the positions of the combination bands.

The infrared and Raman spectra of the carbon dioxide molecule are known with great accuracy, the errors in the positions of the bands being in the neighborhood of 1 or 2 waves per centimeter. The positions of the combination bands predicted by Fermi's theory fail to agree with the observed positions by amounts of the order of 10 to 20 waves per centimeter. Clearly, these discrepancies must be due to the second order corrections to the energy of which no account was taken in Fermi's theory. It is the purpose of the present paper to introduce this second order correction, and to show that with its aid the positions of the observed lines may be predicted with an error no greater than the experimental one. This procedure will allow a determination of the anharmonic force constants which will prove to be of great importance in determining the general form of the potential function of the carbon dioxide molecule.

ANALYSIS

In presenting the analysis we shall use the coordinates q, z, r and φ which were first introduced and fully described by Dennison³ in the discussion of the molecule YX_2 . q measures the relative separation of the oxygen atoms, z the displacement of the carbon atom from the center of mass of the oxygens measured parallel to the line of the latter, while r and φ are the polar coordinates of the carbon in a plane at right angles to the line of the oxygens, the origin of coordinates lying at the intersection.

It proves convenient to introduce the dimensionless variables σ, ξ, ρ and φ instead of q, z, r and φ which are related to them in the following manner:

$$\begin{aligned}\sigma &= 2\pi[\omega_1 m/2h]^{1/2} q, & \xi &= 2\pi[\omega_3 \mu/h]^{1/2} z, \\ \rho &= 2\pi[\omega_2 \mu/h]^{1/2} r, & \varphi &= \varphi.\end{aligned}$$

The Hamiltonian representing the vibrational motion may be readily obtained.⁴ The symmetry of the molecule conditions that the Hamiltonian must be an even function of z and r and independent of φ .⁵

In accordance with the series of approximations to be made on the system, the Hamiltonian may be expanded in a power series in λ , a parameter of smallness.

$$H = H_0 + \lambda H_1 + \lambda^2 H_2.$$

These functions may be quite readily obtained:

$$\begin{aligned}H_0 &\equiv (2\pi^2/h) \{ 2\omega_2 p_\sigma^2 + \omega_3 p_\xi^2 + \omega_2 p_\rho^2 + (\omega_2/\rho^2) p_\varphi^2 \} + (h/2) \{ 2\omega_2 \sigma^2 + \omega_2 \rho^2 + \omega_3 \xi^2 \}, \\ \lambda H_1 &\equiv (2\pi^2 \Delta/h) p_\sigma^2 + h \{ (\Delta/2) \sigma^2 + a \sigma^3 + b \sigma \rho^2 + c \sigma \xi^2 \}, \\ \lambda^2 H_2 &\equiv (\omega_3/2\omega_2 I) \rho^2 p_\xi^2 + h \{ d \sigma^4 + e \rho^4 + f \xi^4 + g \sigma^2 \rho^2 + h \sigma^2 \xi^2 + i \rho^2 \xi^2 \}.\end{aligned}$$

The first order perturbing energy λH_1 contains two classes of terms. The first class represents the fact that ω_1 is not exactly equal to $2\omega_2$, and is proportional to the quantity $\Delta = \omega_1 - 2\omega_2$. In addition to these terms comes the contribution

² D. M. Dennison, Phys. Rev. **41**, 304 (1932).

³ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

⁴ A general treatment of the carbon dioxide molecule would involve the use of a Hamiltonian containing rotational coordinates in addition to the vibrational coordinates. Such a treatment would allow us to obtain not only the rotational energy, but also the interaction between rotation and vibration. This problem will be

from the anharmonic potential; namely, all those terms cubic in the coordinates which fulfill the necessary symmetry conditions.

The second order energy may likewise be divided into two parts, the first of which

reported in a later paper; for the present we restrict ourselves to predicting the centers of the absorption bands.

⁵ Actually the symmetry of the system demands merely that H shall be an even function of z and independent of φ . The fact that we take H to be an even function of r also implies that we assume that H is analytic.

$([\omega_3/2\omega_2 I]\rho^2 p_\xi^2)$ embodies the circumstance that for finite amplitudes of vibration, the molecule deviates slightly from strict linearity. The second part contains the quartic terms of the anharmonic potential of vibration. The solution of the system in zeroth and first approximations has been described in detail elsewhere,² and for our present purpose it will suffice to add only a few points to the results already obtained.

The solution of the zeroth order wave equation may be written in the form

$$\{\partial^2/\partial\rho^2 + (1/\rho)(\partial/\partial\rho) + (1/\rho^2)(\partial^2/\partial\varphi^2) + [(2E/h\omega_2) - \rho^2]\} \Psi_{\rho\varphi} = 0$$

is satisfied by the function (here given in normalized form)

$$R_{(\rho)} V_2 l e^{\pm i l \varphi} = (k!)^{\frac{1}{2}} \{(l+k)!\}^{-\frac{1}{2}} \pi^{-\frac{1}{2}} \rho^l e^{-\rho^2/2} L_{l+k}^l(\rho^2) e^{\pm i l \varphi},$$

where $k = (V_2 - l)/2$. $L_{l+k}^l(\rho^2)$ is the associated Laguerre polynomial of argument ρ^2 , from whose properties it will be comparatively easy to evaluate the necessary matrix elements.

The zeroth order energy constant W_0^n depends only upon the quantum numbers $2V_1 + V_2$ and V_3 , thus showing that in this order of approximation the system is degenerate with respect to the quantum numbers V_1 , V_2 , l . We shall let n represent the former ones and t the additional quantum numbers necessary to define the wave function Ψ_{nt} .

The first order energy constant W_1^{nt} is got by equating the secular determinant $|(H_1)_{nt',n't''} - W_1 \delta_{t',t''}|$ to zero and solving for the roots w_1 . $W_1^{n\tau}$ depends upon the quantum numbers V_1 , V_2 , V_3 , and upon l^2 . It is thus independent of the

$$\Psi_{nt} = \Psi_{(\sigma)}^{V_1} \Psi_{(\xi)}^{V_2} R_{(\rho)}^{V_2 l} e^{\pm i l \varphi}.$$

$\Psi_{(\sigma)}^{V_1}$ and $\Psi_{(\xi)}^{V_2}$ are the well-known Hermitian orthogonal functions with the arguments σ and ξ , respectively. The remaining part $R_{(\rho)}^{V_2 l} e^{\pm i l \varphi}$ has been described as a two-dimensional Hermitian orthogonal function expressed in polar coordinates.³ Since various matrix elements of powers of the coordinates will be required, it will be advantageous to examine this expression in greater detail. It may be shown that the differential equation defining it; namely,

algebraic sign of $\pm l$. This last degeneration is not removed even by the perturbing potential $\lambda^2 H_2$, for $\lambda^2 H_2$ is not a function of the coordinate φ . The appropriate stabilized wave functions for the new levels produced by the first order perturbation are the properly chosen linear combinations $\Psi_{n\tau} = \sum_t C_{\tau t} \Psi_{nt}$, where the $C_{\tau t}$ are given by the first minors of the secular determinant for $W_1^{n\tau}$.

The second order correction to the energy is now determinable in the usual way; that is,

$$W_2^{n\tau} = (H_2)_{n\tau}^{n\tau} + \sum'_{n't'} \{(H_1)_{n\tau}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\},$$

where the dash on the summation sign indicates the omission of those terms for which $n' = n$. This may be expanded into the form:

$$W_2^{n\tau} = \sum_i C_{\tau t_i}^2 [(H_2)_{nt_i}^{nt_i} + \sum'_{n't'} \{(H_1)_{nt_i}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\}] + \\ + \sum_i \sum_j C_{\tau t_i} C_{\tau t_j} [(H_2)_{nt_i}^{nt_j} + \sum' \{(H_1)_{nt_i}^{n't'}\} \{(H_1)_{n't'}^{nt_j}\} / \{W_0^n - W_0^{n'}\}],$$

where the t_1 , t_2 , etc., are the several sets of the degenerate quantum numbers which identify the members of the stabilized wave function. In the case of a triatomic, linear, symmetrical molecule which is not subject to resonance degeneracy, the second order energy constant is given by

$$W_2^{nt} = (H_2)_{nt}^{nt} + \sum'_{n't'} \{(H_1)_{nt}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\}.$$

Unlike the resonance case, in which n comprises

$2V_1 + V_2$ and V_3 , n here refers to V_1 , V_2 , and V_3 as separate entities. The sum in W_2^{nt} is somewhat richer in terms than the corresponding sum

$$\sum'_{n't'} \{(H_1)_{nt_i}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\}$$

in $W_2^{n\tau}$ because of the absence of the resonance phenomenon. Apart from this difference (which proves to be unimportant), it appears that the second order energy constant for the carbon

dioxide molecule may be expressed as a sum of second order energy constants for the nonresonant type of molecule multiplied by the quantities $C_{\tau t_i}^2$, plus terms which cannot be treated in this fashion and which may be called cross products. A very considerable simplification would be effected in the systematics of the problem if it could be shown that the cross products vanish. For, W_2^{nt} modified by the deletion of terms required by the resonance degeneracy is a definite quadratic function of the quantum numbers; namely,

$$h\{x_0 + x_1 V_1 + x_2 V_2 + x_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3\},$$

where the coefficients are known functions of the true anharmonic constants (a, b, c, d, e, f, g, h and i), the fundamental frequencies ($\omega_1, \omega_2, \omega_3$), and the moment of inertia I , and will be enumerated at a later point in the paper. It would thus be possible to write:

$$\lambda^2 W_2^{n\tau} = h \sum_i C_{\tau t_i}^2 \{x_0 + x_1 V_1 + x_2 V_2 + x_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3\}_i.$$

It is obvious that for arbitrarily chosen perturbing potentials λH_1 and $\lambda^2 H_2$, the cross product terms will in general not vanish; and the above equations will not be valid. The perturbing potentials for a molecule of the carbon dioxide type have, however, been assumed to possess certain special properties; namely, they are analytic functions endowed with the geometric sym-

metry of the molecule, λH_1 contains no power greater than the third, and $\lambda^2 H_2$ contains no power higher than the fourth. A detailed study shows that these properties of the potential function cause each of the cross product terms to vanish. The actual proof of this statement will be omitted since the analysis, while quite straightforward, is rather lengthy.

The connection between theory and experiment, and the determination of the anharmonic constants can be facilitated by the consolidation of the energies of the zeroth and second orders. This may be accomplished by means of the relation $\sum_i C_{\tau t_i}^2 = 1$. For, from this it follows at once that $W_0^n = \sum_i C_{\tau t_i}^2 W_0^n$, and hence that

$$W_0^n + \lambda^2 W_2^{n\tau} = h \sum_i C_{\tau t_i}^2 \{x' + \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3\}_i;$$

where

$$x' = x_0 + 2\omega_2 + \omega_3/2,$$

$$\nu_1 = x_1 + 2\omega_2, \quad \nu_2 = x_2 + \omega_2, \quad \nu_3 = x_3 + \omega_3.$$

ω_2 and ω_3 are the zeroth order simple harmonic frequencies which are the solution to the problem of small vibrations.

Omitting the cumbersome details of obtaining the matrix elements⁶ and summing them, the functional dependence of the coefficients may be given as follows. (As listed here the relationships are appropriate for the nonresonant type of triatomic, linearly symmetric molecules, such as CS_2 , and their adaption to CO_2 is achieved by first discarding all terms containing the denominator $\omega_1 - 2\omega_2$, and then replacing ω_1 by $2\omega_2$.)

$$\begin{aligned} x' &= \omega_1/2 + \omega_2 + \omega_3/2 + 3d/4 + 3f/4 + 2e + g/2 + i/2 + h/4 + (11a^2/8 + b^2/2 + c^2/2 + 3ab/2 \\ &\quad + 3ac/4 + bc/2)/\omega_1 + b^2/2(\omega_1 + 2\omega_2) + c^2/4(\omega_1 + 2\omega_3) + h\omega_3/16\pi^2 I\omega_2, \\ \nu_1 &= \omega_1 + 3d/2 + g + h/2 - 3a(9a/8 + b + c)/\omega_1 - 3a^2/8\omega_1 - b^2/2(\omega_1 + 2\omega_2) + b^2/2(\omega_1 - 2\omega_3) \\ &\quad - 3c^2/8(\omega_1 + 2\omega_3) + c^2/4(\omega_1 - 2\omega_3), \\ \nu_2 &= \omega_2 + 3e + g/e + i/2 - b(b + 3a/2)/\omega_1 - b^2/4(\omega_1 + 2\omega_2) + h\omega_3/16\pi^2 I\omega_2, \\ \nu_3 &= \omega_3 + 3f/2 + h/2 + i - c(c + 6a + 4b)/4\omega_1 - 3c^2/8(\omega_1 + 2\omega_3) + c^2/8(\omega_1 - 2\omega_3) + h\omega_3/8\pi^2 I\omega_2, \\ x_{11} &= 3(d - 19a^2/4\omega_1)/2, \end{aligned}$$

⁶ In computing the second order energy constant it is necessary to obtain the matrix elements of the various powers of the coordinates σ, ξ and ρ . These may be readily found by referring to the known properties of the Hermitian and Laguerre orthogonal functions. See for example E. Schrödinger, Ann. d. Physik [4] 80, 437 (1926). Math. appendix, and E. Fues, Ann. d. Physik 80, 367 (1926).

$$\begin{aligned}
x_{22} &= 3e/2 - b^2/2\omega_1 - b^2/8(\omega_1 + 2\omega_2) - b^2/8(\omega_1 - 2\omega_2), \\
x_{33} &= 3f/2 - c^2/2\omega_1 - c^2/8(\omega_1 + 2\omega_3) - c^2/8(\omega_1 - 2\omega_3), \\
x_{11} &= -e/2 + b^2/8(\omega_1 + 2\omega_2) + b^2/8(\omega_1 - 2\omega_2), \\
x_{12} &= g - 3ab/\omega_1 - b^2/4(\omega_1 + 2\omega_2) + b^2/4(\omega_1 - 2\omega_2), \\
x_{13} &= h - 3ac/\omega_1 - 3c^2/8(\omega_1 + 2\omega_3) + c^2/2(\omega_1 - 2\omega_3), \\
x_{23} &= i + h\omega_3/8\pi^2 I\omega_2.
\end{aligned}$$

These equations constitute relations between the constants which fix the energy levels (and which we may hope to obtain from observational data), and the anharmonic constants of the molecule. The question now arises as to whether these equations imply any connections between the x 's and ν 's themselves. We have noticed only one such interdependence, but this will prove to be of considerable value. x_{22} and x_{11} are related through the first order perturbation constant b and the normal frequency ω_2 by the expression $x_{22} + 3x_{11} = -3b^2/16\omega_2$ (this is the form in which it applies to the carbon dioxide molecule). $-3b^2/16\omega_2$ can be reduced to a number directly inasmuch as ω_2 is known to be about 667.5 cm^{-1} while the quite precise value of $|b| = 72.5 \text{ cm}^{-1}$ is given by Dennison.² Thus for the CO_2 molecule $x_{22} + 3x_{11} = -1.47 \text{ cm}^{-1}$. The observational data which help to determine the numerical values of the x 's and ν 's are the experimental locations of the infrared vibration-rotation band centers; for, each such position is given theoretically by the difference between two energies of the type:

$$\begin{aligned}
W_1^{n\tau} + \sum_i C_{\tau i} \{ x' + \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 \\
+ x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 \\
+ x_{23} V_2 V_3 \}_i =
\end{aligned}$$

(Because of the perturbations, the energy of the ground state is raised by the amount $\Delta/2 + x'$.) About half of the extensively known band system of CO_2 is to be employed in this evaluation of the coefficients, and the latter will then be used to predict the remaining known bands as well as bands yet undiscovered. None of the difference bands will be used in the solution, since they yield no independent relations, but only combinations of those obtainable from the fundamentals and their overtones. Hence, the equations to be used in solving for the coefficients will be simply those which give the separations of the

energy levels from the ground state, and they have the form:

$$\begin{aligned}
(W_1^{n\tau} - \Delta/2) + \sum_i C_{\tau i} \{ \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 \\
+ x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 \\
+ x_{23} V_2 V_3 \}_i =
\end{aligned}$$

observed position of level, where $W_1^{n\tau}$ depends upon Δ , l and $|b|$.

We proceed to discuss the adaptation of these equations to the problem of the carbon dioxide molecule.

CORRELATION

The data on the infrared spectrum of CO_2 come from several sources. Barker,⁷ and Martin and Barker⁸ have explored the region between 2.7μ and 15μ , mapping a number of bands which range from the $\nu_3 + (\nu_1, 2\nu_2)$ combination bands to the ν_2 fundamental. Recently, Wu and Barker⁹ have discovered the overtone $3\nu_3$, and have succeeded in getting accurate measurements on the bands $\nu_3 + (4\nu_2, 2\nu_2 + \nu_1, 2\nu_1)$ at 2μ and the bands $\nu_3 + (6\nu_2, 4\nu_2 + \nu_1, 2\nu_2 + 2\nu_1, 3\nu_1)$ at 1.6μ . These new data on the 2μ group of bands displace the older work of Schaefer and Philipps¹⁰ whose measurements appear to be in error by approximately one hundred waves per centimeter. This accounts for the very large discrepancy between the calculated positions of these bands (correct to first order) and the values of Schaefer and Philipps as noted by Dennison.²

Making a tentative solution for the x 's and ν 's on the basis of these observations by Barker, Martin and Wu, it has been demonstrated that the three doublet bands photographed by Adams and Dunham¹¹ in the atmosphere of the planet Venus are indeed to be attributed to the CO_2 molecule and are to be identified as $5\nu_3$ and $5\nu_3 + (\nu_1, 2\nu_2)$. Detailed information concerning all of the known bands of carbon dioxide is collected in Table I together with the names of the observers.

In determining the constants, the x 's and ν 's, it would be possible to equate all the observed

⁷ E. F. Barker, *Astrophys. J.* **55**, 391 (1922).

⁸ P. Martin and E. F. Barker, *Phys. Rev.* **41**, 291 (1932).

⁹ To be published in the near future.

¹⁰ Cl. Schaefer and B. Philipps. *Zeits. f. Physik* **36**, 641 (1926).

¹¹ W. S. Adams and T. Dunham, Jr., *Pub. A.S.P.* **44**, 243 (1932).

positions of the levels to their theoretical values and solve the resulting equations by the method of least squares. This method appears to be impractical, however, for two reasons, first because of the great numerical labor involved and second because, as we shall see, the positions of the levels alone are not suitable for determining certain of the constants with any degree of accuracy. Instead the following method was employed.

Two very significant consequences of Dennison's² first order solution are immediately applicable. The first of these is the very accurate value of $|b|$; and the second is the estimate of Δ . Though Δ may be uncertain in this order of approximation, it is nevertheless of a lesser order of magnitude than $|b|$, and hence than W_1^{nr} . It is thus feasible to expand W_1^{nr} in powers of $\Delta/|b|$, retaining no terms beyond the first power. Direct use is made of this knowledge in simplifying the equations discussed below and in obtaining a preliminary value of Δ for the present solution.

Eleven of the most accurately known and most suitably placed bands are selected in setting up the observational equations, and these together with the relation $x_{22} + 3x_{11} = -1.47 \text{ cm}^{-1}$ give twelve equations in the twelve unknowns: $\nu_1\nu_2\nu_3$; $x_{11}x_{22}x_{33}x_{11}$; $x_{12}x_{13}x_{23}$; $\Delta|b|$. Careful examination shows that this group of equations are algebraically inconsistent with any set of real values for the constants. The difficulty can easily be traced to the quantity Δ which is nearly in-

determinate from the energy levels alone. This is because very small changes in the energy levels (of the order of magnitude of the experimental error) cause large fluctuations in Δ , even allowing it to become imaginary. It was thus necessary to find an alternative method for the definition of the numerical value of Δ , or at least of its order of magnitude. This method is furnished by the ratio of intensities of the strong Raman doublet in CO_2 in the neighborhood of 1300 cm^{-1} . The experimental value of this ratio has been given by Dickinson, Dillon and Rasetti¹² as $2/3$. The amplitudes entering into the intensity expressions for the Raman lines are proportional to the constants C_{rt} ; that is, to the amount in which the wave function active for the Raman effect enters into the wave function of the level in question. The ratio of the intensities is therefore equal to the ratio of the squares of C_{rt} and may be shown in this case to have the form $(1 - \Delta/2^{1/2}|b|)/(1 + \Delta/2^{1/2}|b|)$. In this way it is found that $\Delta \cong 17 \text{ cm}^{-1}$. With this order of magnitude of Δ serving as a criterion, very small (about $\frac{1}{2} \text{ cm}^{-1}$) but arbitrary corrections were made in the observed positions of some of the eleven energy levels mentioned above. These corrections were maintained as small as possible while keeping Δ near 17 cm^{-1} and $|b|$ close to 72.5 cm^{-1} . The modified and now consistent equations are given below, where we have introduced the notation $\beta = |b|$ and $y = \Delta/\beta$.

$$(1) \quad \nu_2 + x_{22} + x_{11} = 667.9 \text{ cm}^{-1},$$

$$(2) \quad \Delta/2 - \beta(1 + y^2/4)/2^{1/2} + (1 - y/2^{1/2})(\nu_1 + x_{11})/2 + (1 + y/2^{1/2})(2\nu_2 + 4x_{22})/2 = 1268.3,$$

$$(3) \quad \Delta/2 + \beta(1 + y^2/4)/2^{1/2} + (1 + y/2^{1/2})(\nu_1 + x_{11})/2 + (1 - y/2^{1/2})(2\nu_2 + 4x_{22})/2 = 1387.9,$$

$$(4) \quad 2\nu_2 + 4x_{22} + 4x_{11} = 1335.8,$$

$$(5) \quad \nu_3 + x_{33} = 2350.1,$$

$$(6) \quad \Delta/2 - \beta(1 + y^2/8) + (1 - y/2)(\nu_1 + x_{11} + \nu_2 + x_{22} + x_{12} + x_{11})/2 + (1 + y/2)(3\nu_2 + 9x_{22} + x_{11})/2 = 1933.2,$$

$$(7) \quad \Delta/2 + \beta(1 + y^2/8) + (1 + y/2)(\nu_1 + x_{11} + \nu_2 + x_{22} + x_{12} + x_{11})/2 + (1 - y/2)(3\nu_2 + 9x_{22} + x_{11})/2 = 2077.4,$$

$$(8) \quad 5\nu_3 + 25x_{33} = 11496.5,$$

$$(9) \quad \Delta/2 - \beta(1 + y^2/4)/2^{1/2} + (1 - y/2^{1/2})(\nu_1 + x_{11} + 5\nu_3 + 25x_{33} + 5x_{13})/2$$

$$+ (1 + y/2^{1/2})(2\nu_2 + 4x_{22} + 5\nu_3 + 25x_{33} + 10x_{23})/2 = 12672.4,$$

¹² Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

$$\begin{aligned}
 (10) \quad & \Delta/2 + \beta(1+y^2/4)/2^{\frac{1}{2}} + (1+y/2^{\frac{1}{2}})(\nu_1 + x_{11} + 5\nu_3 + 25x_{33} + 5x_{13})/2 \\
 & + (1-y/2^{\frac{1}{2}})(2\nu_2 + 4x_{22} + 5\nu_3 + 25x_{33} + 10x_{23})/2 = 12774.7, \\
 (11) \quad & 4\Delta/3 + (4\nu_2 + 16x_{22} + \nu_3 + x_{33} + 4x_{23})/3 + 2(2\nu_1 + \nu_3 + 4x_{11} + x_{33} + 2x_{13})/3 = 4982, \\
 (12) \quad & x_{22} + 3x_{11} = -1.47.
 \end{aligned}$$

These equations yield the following values for the molecular constants.

$$\begin{array}{lll}
 \beta = 72.9 \text{ cm}^{-1} & \nu_3 = 2362.8 & x_{11} = -0.74 \\
 \Delta = 14.7 & x_{11} = -1 & x_{12} = -2.3 \\
 \nu_1 = 1321.7 & x_{22} = +0.74 & x_{13} = -22.1 \\
 \nu_2 = 667.9 & x_{33} = -12.7 & x_{23} = -10.9
 \end{array}$$

While the twelve equations which have been used are consistent and hence yield unique values for the constants, a closer examination discloses the fact that these constants are not determined with equal accuracy. Small changes in the observed positions of the bands (of the order of the experimental error) would sensibly alter some of them, while leaving others virtually unchanged. ν_1 and ν_2 might be out by as much as one wave per centimeter, but ν_3 is probably accurate to about two-tenths of one wave per centimeter. The anharmonic constants β , x_{33} , $x_{13} + 2x_{23}$, and $x_{22} + 3x_{11}$ are known to within a few tenths of one wave per centimeter. The remaining constants are less precisely determined, in some cases only to order of magnitude.

The positions of any of the vibrational levels of the carbon dioxide molecule may now be computed with the aid of the constants just determined. In Table I we have collected the observational data on the positions of the levels in order to compare them with our calculated results. The identification of the levels is given in column I, while the heights of the energy levels above the ground state, observed and calculated, respectively, are contained in columns II and III. The sources of the experimental data are listed in the last column.

In comparing the calculated and observed locations of the vibrational levels, the latter should be divided into two classes. The first of these contains those bands which are employed in the evaluation of the constants; the discrepan-

TABLE I. Observed and calculated values for the energy levels in CO_2 .

Identification $V_1 V_2 V_3 l$	Position (cm^{-1})		Observer (number indicates reference)
	Calculated	Observed	
0 1 0 1	667.9	667.5	8
0 2 0 0	1286.3	1285.8	8
1 0 0 0	1387.9	1388.4	
0 2 0 2	1335.8	1336.2	8
0 3 0 1	1933.2	1933.5	8
1 1 0 1	2077.4	2077.1	
0 0 1 0	2350.1	2350.1	8
0 2 1 0	3614	3610	7
1 0 1 0	3716	3717	
0 4 1 0	4852	4860	9
1 2 1 0	4982	4982	
2 0 1 0	5109	5110	
0 6 1 0	6078	6079	
1 4 1 0	6233	6233	9
2 2 1 0	6352	6353	
3 0 1 0	6512	6512	
0 0 3 0	6974	6978	9
0 0 5 0	11496.5	11496.5	11
0 2 5 0	12672.4	12672.4	11
1 0 5 0	12774.7	12774.7	

cies in this group are all of the order of the experimental error, and represent the small arbitrary additions used to make the simultaneous equations consistent. The agreement between the calculated and observed values for the remaining nine levels is extraordinarily good, being better than the experimental error in eight instances and poorer in only one (the difference of eight waves per centimeter in the case of the 4860 band of the 2μ group of bands is the only example of inferior agreement). This good agreement which obtains in the second class of levels is genuine and not fortuitous. It is to be considered a substantiation of the method of attack used in the problem, and a verification of the expression

TABLE II. Positions of some bands which ought to be accessible to experiment.

Identification V_1 V_2 V_3 l				Calculated position (cm^{-1})
0	2	3	0	8188
1	0	3	0	8291
0	3	4	1	11050
1	1	4	1	11193
0	4	5	0	13823
1	2	5	0	13952
2	0	5	0	14080
0	1	6	1	14322
0	6	5	0	14961
1	4	5	0	15115
2	2	5	0	15234
3	0	5	0	15397
0	0	7	0	15917
0	2	7	0	17049
1	0	7	0	17151
0	0	9	0	20236
0	2	9	0	21324
1	0	9	0	21426

for the energy of the carbon dioxide molecule.¹³

In Table II are given the positions of some bands which ought to be accessible to experiment, but which have as yet not been discovered. The bands in the visible and photographic infrared regions of the spectrum will have to be sought in the absorption spectrum of the planet Venus, and such a search is being made by T. Dunham, Jr., at Mount Wilson Observatory. On the other hand, the bands $3\nu_3 + (\nu_1, 2\nu_2)$ should offer no par-

ticular difficulty, and should be as easily observed as the bands at 1.6μ .

CONCLUSION

The second order energy constant for the carbon dioxide molecule has been computed. It involves eleven constants whose connections with the twelve constants defined by the potential energy is given. It is consequently not possible to obtain the potential energy function from our present results, and recourse must be had to some alternative method. This method consists in an analysis of the interaction between vibration and rotation. It may be shown that the convergence in the fine structure lines of the various absorption bands will yield values for the three constants of the first order potential function; namely, a , b and c . A determination of the entire potential function is thus made possible. This investigation will be the subject of a second paper, to appear, shortly in which, also, an attempt will be made to describe the potential energy of the carbon dioxide molecule by means of a function resembling the Morse potential function for diatomic molecules.

Finally, the writers wish to express their indebtedness and thanks to Professor E. F. Barker and Mr. Ta-You Wu for placing the results of their investigation at our disposal and allowing us to publish a preliminary account of them, and to Dr. T. Dunham, Jr. for his willing and helpful correspondence in connection with the Venus bands.

¹³ In a recent paper Langseth and Nielsen (Zeits. f. physik. Chemie B19, 427 (1932)), have reexamined the Raman spectrum of gaseous carbon dioxide, using an exposure time of one month. In addition to the four Raman lines previously known, they obtained six very faint lines which should, presumably, be due to transitions starting from the three excited levels in the neighborhood of 1300 cm^{-1} . The observed positions of the six extremely faint lines are: 1241, 1305, 1325, 1344, 1369 and 1433 cm^{-1} . On the other hand, the frequencies of the above-mentioned transitions may be readily computed from our formulae, and eight very faint Raman lines should appear in the following positions: 1166, 1248, 1268, 1288, 1390, 1415, 1426 and 1517 cm^{-1} . It thus appears that of the eight lines

which should appear, the lines 1268, 1288, 1390 and 1415 blend with the four already known Raman lines; the lines 1166 and 1517 do not fall within the limits of the region covered by the experimental data, while the lines 1248 and 1426 probably correspond to the two observed lines 1241 and 1433. The lines 1241 and 1433 are classified as *ausserordentlich schwach* and hence the discrepancy between the observed and computed values is not to be considered as a serious disagreement. There appears to be no place in the theoretical scheme for the remaining four observed lines, inasmuch as we have been able to find no transitions corresponding to these frequencies. It is perhaps possible that this discrepancy originates in the intrinsic difficulty experienced in recording faint lines through exposures of such extended duration.

The Infrared Spectrum of Carbon Dioxide. Part II

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The interaction between the vibration and rotation of the CO_2 molecule is discussed. It is shown that the fine-structure lines will exhibit a convergence which depends upon certain of the anharmonic potential constants. The convergence factors are compared with the experimental data of the resolved bands and an excellent agreement is found, which leads to a determination of the anharmonic constants. Combining these results with those of Part I,

the complete potential function for CO_2 is obtained. A simple analytic function for the potential is proposed which contains but four constants. It is shown that this function agrees satisfactorily with the experimental potential for small displacements. The range of the validity of the analytic function is discussed and one of the heats of dissociation of CO_2 is obtained.

INTRODUCTION

A PREVIOUS paper by this title, Part I,¹ was concerned with an analysis of the vibrational levels of the linear and symmetrical molecule O—C—O . The Hamiltonian governing the vibrational motions of the molecule was shown to have the form,

$$H = H_0 + \lambda H_1 + \lambda^2 H_2,$$

where

$$\begin{aligned} H_0 &\equiv (2\pi^2/\hbar) \{ 2\omega_2 p_\sigma^2 + \omega_2 p_\rho^2 + \omega_3 p_\xi^2 + (\omega_2/\rho^2) p_\varphi^2 \} \\ &\quad + (\hbar/2) \{ 2\omega_2 \sigma^2 + \omega_2 \rho^2 + \omega_3 \xi^2 \}, \\ \lambda H_1 &\equiv (2\pi^2\Delta/\hbar) p_\sigma^2 + \hbar \{ (\Delta/2) \sigma^2 + a\sigma^3 + b\sigma\rho^2 + c\sigma\xi^2 \}, \\ \lambda^2 H_2 &\equiv (\omega_3/2\omega_2 I) \rho^2 p_\xi^2 \\ &\quad + \hbar \{ d\sigma^4 + e\rho^4 + f\xi^4 + g\sigma^2\rho^2 + h\sigma^2\xi^2 + i\rho^2\xi^2 \}. \end{aligned}$$

The quantities σ , ρ , and ξ are dimensionless variables corresponding to the normal coordinates q , r , and z , respectively.

A system having the Hamiltonian H_0 was solved rigorously and to this system, λH_1 and $\lambda^2 H_2$ were applied as first and second order perturbations. An expression was thus obtained for the vibrational energy levels $W = W_0 + \lambda W_1 + \lambda^2 W_2$ which was shown to be in excellent agreement with the observed positions of the levels.

The immediate dependence of the energy W was upon eleven derived constants whose connections with the twelve constants of H were

given explicitly. Thus the positions of the vibrational levels furnish but eleven data and it is necessary to find some new relation before the twelve constants of the potential energy may be determined. This new relation may be found from an analysis of the interaction between the vibration and rotation of the molecule. It will be shown that this interaction, just as in the case of a diatomic molecule, leads to a convergence in the band lines; that is, to a term in the fine-structure formula proportional to the square of the ordinal number of the line. The analysis, in addition to fixing the values of the twelve energy constants, serves to correlate the convergence factors of all the CO_2 bands which have thus far been resolved.

THE INTERACTION BETWEEN ROTATION AND VIBRATION

The interaction between vibration and rotation can be divided into two parts which may be described in the following way. The centrifugal forces occasioned by the rotation of the molecule pull the atoms away from their old equilibrium positions to new ones in the anharmonic force field. The frequencies with which the atoms oscillate about their new positions of rest differ from the corresponding frequencies of the non-rotating molecule by amounts which are measured by the anharmonicity of the field; that is, in first order by the coefficients a , b and c , and in higher order by d , e , f , g , h and i . It is thus

¹ Adel and Dennison, Phys. Rev. **43**, 716 (1933).

apparent that the frequencies of vibration are slightly dependent upon the rotational state of the molecule, giving rise to a convergence factor in the fine-structure formula. This part of the mutual perturbations may be thought of as the effect of rotation upon vibration.

The reverse phenomenon; namely, the perturbation of rotation by vibration is independent of the anharmonic nature of the force field. To the present degree of approximation, the moments of inertia of the molecule must be considered as functions of the normal coordinates. The consequent periodic fluctuation of the moments of inertia distorts the rotational frequency to a new value. It is clear that this mechanism also induces a convergence of fine-structure lines. It is to be noted that a consequence of the effect of the vibration is to distort the molecule into a slightly asymmetrical rotator with three different, and in this instance variable, moments of inertia.

The three moments of inertia of the molecule depend upon the normal coordinates in the following manner,

$$C = \mu r^2, \quad B = (m/2)(a+q)^2 + \mu z^2, \quad A = B + C.$$

The wave equation describing the system may be easily obtained. It consists of two parts. The first of these is independent of the rotation and was the equation treated in Part I. The second part of the wave equation contains terms relating both to the rotation of the molecule and to the interaction between vibration and rotation. It may be written,

$$\begin{aligned} & [\partial^2/\partial\vartheta^2 + \cot\vartheta(\partial/\partial\vartheta) + (A_e/C_e + \cot^2\vartheta)\partial^2/\partial\varphi^2 \\ & + \csc^2\vartheta(\partial^2/\partial\psi^2) - 2\cot\vartheta\csc\vartheta(\partial^2/\partial\varphi\partial\psi) \\ & + 8\pi^2 A_e W/h^2] U + (\mu r^2/I) F(\varphi, \vartheta, \psi; \partial^2/\partial\vartheta^2, \\ & \partial^2/\partial\varphi^2, \partial^2/\partial\psi^2; \partial^2/\partial\vartheta\partial\varphi, \partial^2/\partial\vartheta\partial\psi, \partial^2/\partial\varphi\partial\psi) U \\ & = 0, \end{aligned}$$

where $1/A_e = \frac{1}{2}(1/A + 1/B)$ and $1/C_e = 1/C - \frac{1}{2}(1/A + 1/B)$. It is evident that the first group of terms constitute the wave equation for a symmetrical rotator with effective moments of inertia A_e and C_e . The remaining terms, grouped as $(\mu r^2/I)F$, have no counterpart in the symmetrical rotator equation and are the purely asymmetrical rotator terms. These terms would

introduce effects characteristic of the difference between the energy levels of the symmetrical and asymmetrical rotators. They would give rise to a splitting of the fine-structure lines into multiplets whose separation would be a function of the small coefficient $(\mu r^2/I)$. The bands of CO_2 observed in the Venus atmosphere are very finely resolved but they show no trace of multiplicity or even of unsharpness. We may, therefore, on purely *a priori* grounds discard the group of terms $(\mu r^2/I)F$. An exact analysis, moreover, confirms this conclusion and shows that they will, to the present order of approximation, furnish no contribution to the energy levels.

The wave equation involving the angles ϑ, φ, ψ may now be integrated and we can show that the interaction energy (and hence the convergence) may be considered as due wholly to those terms which mark the difference between the symmetrical rotator with effective moments of inertia A_e and C_e and the rigid, linear model of CO_2 with moment of inertia I . Expanding $1/A_e$ and $1/C_e$ in powers of the normal coordinates we may, upon introduction of the quantum numbers of angular momentum J and l , express the interaction in the form of a perturbing potential energy.

$$V_I = \frac{h^2}{8\pi^2 I} [J(J+1) - l^2] \left[\frac{-3q^2}{a^2} + \frac{\mu}{I}(r^2 + z^2) + \frac{2q}{a} \right].$$

The most significant term is the one linear in q , for it marks the removal of the oxygen atoms to new positions of equilibrium. As will become evident, it is immediately responsible for the introduction of the anharmonic coefficients a, b and c . The terms, quadratic in q, r and z giving the remainder of the interaction, express the variation of the principal moments of inertia with the phase of vibration.

When considered as a portion of the potential energy of the molecule, V_I is inconsistent with the assumption of normal coordinates because of the presence of the stretching term proportional to q . A transformation must, therefore, be effected from the coordinate q to a normal coordinate x . q and x satisfy the relation $q - x = \delta$, where

$$\delta = (h^2/8\pi^2 I)(J(J+1) - l^2)/4\pi^2\omega_2^2(2Im)^{\frac{1}{2}}$$

is the linear displacement of equilibrium. Transforming the cubic anharmonic potential from its dependence upon q to its new dependence upon x , we find the final form of the interaction function to be,

$$V_I = -(h^2/8\pi^2 I)[J(J+1) - l^2][-3(m/2I + \alpha/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})x^2 + (\mu/I - \beta/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})r^2 + (\mu/I - \gamma/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})z^2],$$

where

$$\alpha x^3 = a\sigma^3, \quad \beta xr^2 = b\sigma\rho^2, \quad \gamma xz^2 = c\sigma\xi^2.$$

That is to say, we have $V_I = C_1\sigma^2 + C_2\rho^2 + C_3\xi^2$ and as a consequence the correction to the energy of a rotation vibration level can be found from the zeroth order energy of vibration of the molecule by a comparison of the coefficients in V_I with the corresponding coefficients in

$$V_0 = (h/2)(2\omega_2\sigma^2 + \omega_2\rho^2 + \omega_3\xi^2).$$

In other words, since the contribution of V_0 is

$$h\{2\omega_2(V_1 + \frac{1}{2}) + \omega_2(V_2 + 1) + \omega_3(V_3 + \frac{1}{2})\},$$

the contribution of V_I is

$$E_I = (h^2/8\pi^2 I)[J(J+1) - l^2][(V_1 + \frac{1}{2})\{3h/8\pi^2 I\omega_2 + (3h/4\pi^2 m\omega_2)(\alpha/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})\} + (V_2 + 1)\{-h/4\pi^2 I\omega_2 + (h/4\pi^2 \mu\omega_2)(\beta/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})\} + (V_3 + \frac{1}{2})\{-h/4\pi^2 I\omega_3 + (h/4\pi^2 \mu\omega_2)(\gamma/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})\}].$$

We have now computed the energy shift of a rotation-vibration level resulting from the interaction between rotation and vibration. To pass from the corrected energy levels to the corrected positions of the fine-structure lines the selection rules for J and l must be introduced. For a parallel band $\Delta J = \pm 1$ and $\Delta l = 0$. Representing by N the ordinal number of the fine-structure line, the correction to the N -th line of a parallel band produced in a transition from the ground state is

$$\Delta\nu = (h/8\pi^2 Ic)[\{P V_1 + Q V_2 + R V_3\} N^2 + \{P(V_1 + 1) + Q(V_2 + 2) + R(V_3 + 1)\} N],$$

where P , Q , and R are the respective coefficients of $(V_1 + \frac{1}{2})$, $(V_2 + 1)$, and $(V_3 + \frac{1}{2})$ within the bracket $[]$ of the above expression for E_I . Similar expressions obtain for the corrections to the fine-structure of a perpendicular band.

The interpretation of $\Delta\nu$ follows at once from a correlation with the empirical expression for the positions of the fine-structure lines in a band. In the empirical formula $\nu = K_0 + K_1 N + K_2 N^2$, K_1 is the major interval between fine-structure lines, while K_2 fixes the convergence which is superimposed upon the spacing determined by K_1 . This suggests the division of $\Delta\nu$ into two sections—the one linear and the other quadratic in N . That is to say, the interaction between rotation and vibration not only is the cause of convergence, but it alters the major interval as well. Thus, the measured separation of lines is

$$K_1 = h/4\pi^2 Ic + \text{linear part of } \Delta\nu.$$

The quantity $\Delta\nu$ is, therefore, essential to a precise determination of the moment of inertia of the molecule.

Putting the numerical values of the known constants into $\Delta\nu$, we find:

$$\begin{aligned} \Delta\nu = & 0.390[(0.00175 + 0.000112a) V_1 + (-0.00117 + 0.0000372b) V_2 \\ & + (-0.00033 + 0.000019c) V_3] N^2 + 0.390[(0.00175 + 0.000112a)(V_1 + 1) \\ & + (-0.00117 + 0.0000372b)(V_2 + 2) + (-0.00033 + 0.000019c)(V_3 + 1)] N. \end{aligned}$$

Of the twenty-eight bands which have now been observed in the infrared spectrum of carbon dioxide, only five are sufficiently well resolved for the present analysis. These are the active fundamentals and the three Venus bands. The observed positions are:²

$$\begin{aligned} \nu_2 &= 667.5 + 0.780 N + 0.0005 N^2; & \nu_3 &= 2350.1 + 0.780 N - 0.0035 N^2; \\ 5\nu_3 &= 11496.5 + 0.769 N - 0.0153 N^2; & 5\nu_3 + (\nu_1, 2\nu_2) &\begin{cases} 12672.5 + 0.769 N - 0.0150 N^2 \\ 12774.7 + 0.769 N - 0.0156 N^2. \end{cases} \end{aligned}$$

(For sources of data see Part I.)

The band ν_2 possesses the theoretical convergence: $0.390(-0.00117 + 0.0000372b)N^2$. From the vibrational analysis of Part I the value 72.9 cm^{-1} was obtained for $|b|$. Obviously the convergence demands that b be positive and the value $b = 72.9 \text{ cm}^{-1}$ yields the convergence factor $+0.0006 N^2$, in excellent agreement with the observed value $+0.0005 N^2$.

Of the two bands ν_3 and $5\nu_3$, the photographic one, $5\nu_3$, is the more accurately resolved. For this reason $5\nu_3$ will be used to compute the value of c which will then serve to predict the convergence of the fundamental ν_3 . From the equation

$$0.390(-0.00033 + 0.000019c)5 N^2 \text{ cm}^{-1} = -0.0153 N^2 \text{ cm}^{-1}$$

the value $c = -202.1 \text{ cm}^{-1}$ is found. The calculated convergence $-0.0031 N^2$ agrees very well with the measured value $-0.0035 N^2$ for the ν_3 fundamental.

The convergences for the combination bands at $12,672.5$ and $12,774.7 \text{ cm}^{-1}$ are given by the respective linear combinations:

$$\begin{aligned} &\{0.43[0.390(0.00175 + 0.000112a)] \\ &\quad + 0.57(0.00120) - 0.0153\} N^2 \\ &\{0.57[0.390(0.00175 + 0.000112a)] \\ &\quad + 0.43(0.00120) - 0.0153\} N^2 \end{aligned}$$

since the resonance degeneracy of the molecule described in Part I must be taken into account. Equating the first expression to the observed datum $-0.0150 N^2$, the value -36.2 cm^{-1} for the anharmonic constant a is found. When this is substituted into the second expression the value

$-0.0153 N^2$ is obtained, which may be compared with the observed constant $-0.0156 N^2$.³

The moment of inertia of CO_2 may be determined from any of the resolved infrared bands. It appears, however, that the $5\nu_3$ band should yield the most reliable value since it is the most accurately resolved band. In making the computation the correction arising from the convergence factor must be applied to the coefficient of N in the fine-structure formula. The observed major interval of the $5\nu_3$ band is 0.769 cm^{-1} . It follows that:

$$0.769 N = hN/4\pi^2 Ic - 0.0031(V_3 + 1)N,$$

where $V_3 = 5$. We obtain $I = 70.1 \times 10^{-40} \text{ gram cm}^2$, a value which is in good accord with the value 70.2×10^{-40} as determined from the rotational Raman effect of CO_2 .⁴

THE POTENTIAL ENERGY FUNCTION OF CO_2

The analysis of the interaction between rotation and vibration has yielded values for the coefficients a and c . Combining these data with the x 's and ν 's it becomes possible to determine the remaining anharmonic coefficients; namely, d, e, f, g, h, i . The equations used in this evaluation are given on pages 719 and 720 of Part I and are simply the connections between the constants of the vibrational energy and the constants of the vibrational potential. The results of this calculation are listed in Table I, together with the zeroth and first order constants of the potential.

$\omega_1, \omega_2, \omega_3, b$, and c are the most accurately known of the twelve constants, with a probable

³ We are very much indebted to Professor E. F. Barker for the following information. He has recently resolved the two infrared bands $\nu_3 - (\nu_1, 2\nu_2)$ at 10μ , and from the convergence factors which he obtains, the two values of a $-38.6, -36.6$ may be computed. We shall adopt the mean value -37.0 .

⁴ Houston and Lewis, Proc. Nat. Acad. **17**, 229 (1931).

² Due to the fact that the oxygen nucleus has zero spin, half of the fine-structure lines of CO_2 are missing. The above formulae represent the observed positions of the lines when N takes on the values $+1, +3, +5, +7$, R -branch; $-2, -4, -6, -8$, P -branch.

TABLE I.

ω_1 1361 cm ⁻¹	a -48.8	d 7.8, 5.3	g -9.9
ω_2 673	b 72.9	e 2.0	h 7.7
ω_3 2378	c -202.1	f 2.4	i -12.3

error of about $\frac{1}{2}$ percent. The value of a is probably known to within 5 percent while the remaining constants may well be in error by as much as 10 percent to 15 percent. Two values are given for d , one obtained from the constant x_{11} and the other from the expression for ν_1 . We should regard the latter determination as the more accurate. It is to be noted that the least accurately known constants are the smallest in magnitude; namely, the coefficients of the second order potential. The behavior of the molecule, however, is determined chiefly by the zeroth and first order potentials. Consequently, we believe that the potential energy of the carbon dioxide molecule for small displacements will be represented to within a few wave numbers by the data in Table I. An attempt will now be made to approximate this potential energy by means of an analytic function with a fewer number of constants.

It seems probable that each of the two oxygen nuclei are bound to the carbon nucleus by a force field having a potential minimum. The success of the Morse potential function for diatomic molecules suggests that we connect the carbon with each of the oxygens by a Morse function. The constants of these two functions will, of course, be identical. The valencies of the two oxygen atoms are satisfied by the carbon atom and we might accordingly expect that the two oxygen atoms will repel one another. From analogy with the repulsion forces of homopolar atoms we shall attempt to approximate this potential by an expression of the form Ae^{-Bq} . Thus,

$$V = [De^{-2\alpha(r_1+\epsilon)} - 2De^{-\alpha(r_1+\epsilon)}] \\ + [De^{-2\alpha(r_2+\epsilon)} - 2De^{-\alpha(r_2+\epsilon)}] + Ae^{-Bq}.$$

The distances between the nuclei are given by $a/2+r_1$, $a/2+r_2$, and $a+q$, as shown in Fig. 1,

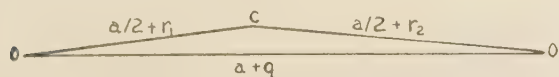


FIG. 1. Configuration of the carbon dioxide molecule.

and completely define the configuration of the system. The quantities r_1 and r_2 are connected with the normal coordinates by the relations

$$r_1 = q/2 + r^2/a + z, \quad r_2 = q/2 + r^2/a - z$$

and V may be rewritten as follows, where $y = q/2 + r^2/a$,

$$V = 2De^{-\alpha(\epsilon+y)} \cosh 2\alpha z \\ - 4De^{-\alpha(\epsilon+y)} \cosh \alpha z + Ae^{-Bq}.$$

The equilibrium condition

$$\partial V/\partial q = \partial V/\partial r = \partial V/\partial z = 0 \quad \text{at} \quad q=r=z=0$$

yields the relation $2\alpha^2\epsilon D = AB$. ϵ can thus be evaluated in terms of α , D , A and B , and the potential V is seen to depend upon these four parameters only.

For the purpose of comparison with the terms of the series potential already obtained for CO_2 , we must expand $V(r_1r_2q)$ about the point $q=r=z=0$, and all terms through the quartic must be retained. Powers of ϵ higher than the first may be neglected, and the expansion yields the following term by term comparison,

$$\pi^2 m \omega_1^2 = \frac{1}{2} \{ AB^2 + D\alpha^2(1-3\alpha\epsilon) \},$$

$$2\pi^2 \mu \omega_2^2 = 4\epsilon D\alpha^2/a,$$

$$2\pi^2 \mu \omega_3^2 = 2D\alpha^2(1-3\alpha\epsilon),$$

$$a = \{ (D\alpha^3/4) [(7\alpha\epsilon/3) - AB^3/6] \} R^3,$$

$$b = \{ 2D\alpha^2(1-3\alpha\epsilon)/a \} RS^2,$$

$$c = \{ D\alpha^3(7\alpha\epsilon-3) \} RT^2,$$

$$d = \{ AB^4/24 + (D\alpha^4/96)(7-15\alpha\epsilon) \} R^4,$$

$$e = \{ 2D\alpha^2(1-3\alpha\epsilon)/a^2 \} S^4,$$

$$f = \{ D\alpha^4(7-15\alpha\epsilon)/6 \} T^4,$$

$$g = \{ D\alpha^3(7\alpha\epsilon-3)/2a \} R^2S^2,$$

$$h = \{ D\alpha^4(7-15\alpha\epsilon)/4 \} R^2T^2,$$

$$i = \{ 2D\alpha^3(7\alpha\epsilon-3)/a \} S^2T^2, \text{ where}$$

$$R = (1/2\pi) [h/m\omega_2]^{\frac{1}{2}},$$

$$S = (1/2\pi) [h/\mu\omega_2]^{\frac{1}{2}},$$

$$T = (1/2\pi) [h/\mu\omega_3]^{\frac{1}{2}}.$$

For the determination of α , D , B and A , it is desirable to employ the four best known of the

constants $\omega_1 \dots i$. ω_1 , ω_2 , ω_3 and c are evidently the data required. (The constant b is unsuited for the fourth relation as will be seen in the general discussion to follow.) In this way we obtain,

$$\alpha = 1.81A^{-1}, \quad B = 1.086A^{-1}, \quad \epsilon = 0.061A.$$

$$D = 168350 \text{ cm}^{-1}, \quad A = 62600 \text{ cm}^{-1}.$$

By using these values, the remaining anharmonic constants can be predicted and the suitability of the generalized Morse function will be indicated by the agreement between these values and the corresponding ones obtained earlier in the paper. The comparison is contained in Table II.

TABLE II.

	Infrared analysis	Generalized Morse function
a	-37.0 cm^{-1}	-36 cm^{-1}
b	72.9	102
d	5.3, 7.8	1.1
e	2.0	4.6
f	2.4	4.1
g	-9.9	-8.9
h	7.7	12.4
i	-12.3	-17.7

The agreement shown in Table II is, in several respects, satisfactory. The anharmonic constants are correctly given by $V(r_1r_2q)$ as regards order of magnitude and as regards algebraic sign. It is apparent, however, that their numerical values diverge by amounts which are certainly in excess of the experimental errors. Perhaps the principal objection to the function we have chosen is that it belongs to the class of central force potentials which have, in the past, shown themselves to be incapable of describing the potential functions of polyatomic molecules. There are certain consequences of the central force assumption which are completely independent of the restricted form $V(r_1r_2q)$. This assumption imposes certain restrictions upon the anharmonic constants which are listed below:

$$b/\omega_3^2 = 2\pi^2\mu RS^2/a; \quad e/\omega_3^2 = 2\pi^2\mu S^4/a^2$$

$$i/g = 4T^2/R^2; \quad f/h = 2T^2/3R^2.$$

It is because b is already specified by the central character of the forces that it may not be used in determining the constants of the generalized Morse function.

The fact that the four relations given above are not accurately fulfilled by the actual constants of the molecule proves that the true force function cannot be wholly central in character. On the other hand, the fact that they are approximately fulfilled leads us to the belief that to this extent the potential energy of CO_2 can be represented by a central force function such as $V(r_1r_2q)$.

Our purpose in introducing $V(r_1r_2q)$ was to find a function which possesses definite physical significance and whose constants might be evaluated from the infrared data. The function we have chosen does fairly well represent the potential energy of CO_2 for small displacements of the particles. The question now arises as to whether it will also furnish some measure of the potential for large displacements and of the heats of dissociation of the molecule.

Suppose, for example, that we consider the dissociation of CO_2 into CO and O , where we must suppose that the products of the dissociation are probably not in the normal state. For this purpose we assume that one of the oxygen atoms is slowly removed to infinity; the distance between the remaining C and O remaining constant. This can be accomplished by letting q and z become infinite while preserving the relation $z=q/2$. The energy required for this operation is $D-A$, but the residual CO molecule is not in its normal state since $a/2$ is no longer its equilibrium distance, but rather $(a/2)-\epsilon$. The heat of dissociation is thus equal to

$$2De^{-\alpha\epsilon} - De^{-2\alpha\epsilon} - A.$$

Upon substituting the values of the constants, we obtain for the heat of dissociation 103,750 cm^{-1} or 300 calories/mol. In order to compare this figure with an experimental determination of the heat of dissociation we would require more detailed information about the excited states of CO and O than appears to be now available.

